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(54) MANUFACTURE OF FLAT BATTERY POSTITIVE ELECTRODE

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a positive electrode free from deformation or warping by mixing a powdery positive electrode active material with a positive electrode conductive material to prepare a positive electrode mix, forming a mixed solution of a dispersion solution of an tetrafluoroethylene resin and a dispersion solution of a tetrafluoroethylene haxafluoropropylene copolymer resin, mixing the positive electrode mix therewith followed by drying, and filling the resulting mixture in a die as a granular mix to form a pellet.
SOLUTION: Powdery baked MnO2 and powdery graphite are used as positive electrode active material and a conductive material, respectively. For example, the graphite powder is mixed in the ratio of 6 pts.wt. to 94 pts.wt. of the baked MnO2 to prepare a positive electrode mix. In parallel to this preparation, a binder is prepared. Twenty grams of a dispersion solution of an aqueous tetrafluoroethylene resin containing a solid component in a ratio of 60 wt.% is mixed with 20 g of a dispersion solution of an aqueous tetrafluoroethylene- propylene hexafluoropropylene copolymer resin containing a solid component in a ratio of 50 wt.% followed by stirring to prepare a mixed solution. Thereafter, 200 cc of water is further added thereto followed by sufficient mixing, and the resulting mixture is added to the positive electrode mix and kneaded.

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CLAIMS

[Claim(s)]
[Claim 1] positive active material and the positive-electrode conductivity matter which makes a graphite a subject -- mixing -- a positive electrode -- with the process which forms a mixture, and the solution with which polytetrafluoroethylene resin was distributed Mix the solution with which fluorinated ethylene-propylene copolymer was distributed, and it considers as a mixed solution. It adds to a mixture. the process which adds water to this mixed solution and is further mixed to it, and the mixed solution with which water was added -- this positive electrode -- a positive electrode -- the process which kneads a mixture, and the kneaded positive electrode -- a mixture -- granulation -- drying -- granularity -- the process used as a mixture, and granularity -- the process which carries out pressing and forms the positive electrode of a pellet type after filling up a mold with a mixture -- since -- the manufacturing method of the becoming positive electrode for flat form cells.
[Claim 2] The manufacturing method of the positive electrode for flat form cells according to claim 1 whose weight ratio of the fluorinated ethylene-propylene copolymer to positive active material and the positive-electrode conductivity matter is 0.5 - 6 % of the weight.
[Claim 3] granularity -- the manufacturing method of the positive electrode for flat form cells according to claim 1 whose particle size of a mixture is 50-1000 micrometers.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the manufacturing method of the positive electrode for flat form cells which controls generating of the crack in the front face and the interior of a pellet type positive electrode, or a chip in detail about the manufacturing method of the cell which held the generation-of-electrical-energy element containing the positive electrode fabricated by the pellet type in the cell container of a flat form.

[0002]
[Description of the Prior Art] Since the obturation plate which serves as a negative-electrode terminal the generation-of-electrical-energy element which consists of the electrolytic solution using the negative electrode and organic electrolyte using a positive electrode, a lithium, or its alloy, and the flat form organic electrolyte cell held in the cell container of the flat form which consists of a cell case which serves both as a positive-electrode terminal use a lithium for a negative-electrode active material, it has the description that an energy density is high. A miniaturization and lightweight-izing of a device are not only possible, but since it has high-reliability, this kind of cell is used as the main power supply and memory backup power supply of various electronic equipment.
[0003]
[Problem(s) to be Solved by the Invention] the positive electrode which mixed the powder of positive active material, such as a conductive manganese dioxide, and conductive matter, such as carbon, with which the positive electrode of such a flat form organic electrolytic-solution cell makes a subject positive active material and the conductive matter -- a mixture -- granulation and desiccation -- carrying out -- granularity -- after considering as a mixture, it is created by the approach which a pellet type is made to fabricate by filling up a mold with this and pressurizing it. The positive electrode of a pellet type has the low binding capacity between powder which is fabricating the mixture only by application of pressure and constitutes a mixture. For this reason, a crack will arise on the interior and the front face of a pellet by the chip from which a part of pellet breaks and falls by the oscillation in a production process, contact to equipment, or the collision between pellet type positive electrodes, and desiccation after shaping. in order to prevent generating of such nonconformity -- a positive electrode -- while raising the viscosity of a mixture, it is necessary to make the binding capacity of fine particles increase then, the dispersion solution which distributed polytetrafluoroethylene resin (PTFE) in the solvent as a thickener and a binder -- a positive electrode -- after kneading in addition to a mixture, the approach of fabricating to a pellet type is used. (It indicates to JP,55-93671,A and JP,55-96557,A) the above-mentioned approach -- a positive electrode -- generating of said chip and crack decreases in the manufacturing method which added the solution which made the mixture distribute polytetrafluoroethylene resin. However, when the solution containing polytetrafluoroethylene resin dries after fabricating to a pellet type, deformation and curvature return will arise. In case the generation-of-electrical-energy element containing such a positive electrode is held in the cell container of a flat form using feeders, such as a parts feeder, the part which the deformation and the curvature in the positive electrode of a pellet type produced is caught inside a feeder, and causes [that it can set like a cell assembler] a trouble.
[0004] This invention does not have generating of a crack or a chip in a pellet, and aims at offering the positive electrode which neither deformation nor curvature produces further.
[0005]

[Means for Solving the Problem] In order to attain the above-mentioned object, the manufacturing method of the positive electrode for flat form cells of this invention As opposed to a mixture the positive electrode which mixed the graphite which exists in the shape of powder as well as powder-like positive active material, and is used as the conductive matter -- To the mixed solution with which the solution with which polytetrafluoroethylene resin was distributed, and the solution with which fluorinated ethylene-propylene copolymer was distributed were mixed beforehand The point using the solution with which the solution which furthermore added water is added and fluorinated ethylene-propylene copolymer was distributed, the mixed solution which mixed beforehand each solution with which polytetrafluoroethylene resin and fluorinated ethylene-propylene copolymer were distributed -- a positive electrode -- it is characterized by the point added to a mixture.

[0006]

[Embodiment of the Invention] Hereafter, the operation gestalt of this invention is explained.

[0007] The manufacturing method of the positive electrode for flat form cells concerning this invention includes each process shown below. (1) the positive-electrode conductivity matter which exists the positive active material which exists in the shape of powder, and in the shape of powder, and makes a graphite a subject -- mixing -- a positive electrode -- the process which adjusts a mixture, and (2) With the solution with which polytetrafluoroethylene resin was distributed [namely,] A mixed solution with the solution with which fluorinated ethylene-propylene copolymer was distributed is created. the process further mixed after adding water to this mixed solution, and (3) It adds to a mixture. the mixed solution with which water was added -- a positive electrode -- a positive electrode -- the process which kneads a mixture, and (4) the kneaded positive electrode -- a mixture -- granulation -- drying -- granularity -- the process used as a mixture, and (5) granularity -- the process which carries out pressing and forms the positive electrode of a pellet type after filling up a mold with a mixture -- since -- it becomes.

[0008] According to the aforementioned manufacturing method, polytetrafluoroethylene resin and fluorinated ethylene-propylene copolymer are used as a binder of a positive electrode, and the binding capacity of positive active material and conductive material improves compared with the case where these are used independently. this -- granularity -- the chip of a pellet and the occurrence frequency of a crack in the phase which pressurizes and fabricates a mixture fall substantially. Furthermore, in the process which supplies the fabricated positive electrode of a pellet type to a positive-electrode container using feeders, such as a parts feeder, deformation, such as change of a positive-electrode configuration, curvature [in / specifically / a pellet principal plane], or crushing, is not produced. Furthermore, it can contribute to the operation by which the connection inside the feeder by deformation or curvature did not arise, and the manufacturing installation was stabilized.

[0009] moreover, the solution with which each resin was distributed -- a positive electrode -- the mixed solution which added water to this further after mixing the solution with which it did not add separately to the mixture, but each resin was distributed beforehand -- carrying out -- this mixed solution -- a positive electrode -- it has added to the mixture. this time -- a positive electrode -- a mixture -- the positive electrode of the binder which becomes inside from each aforementioned resin -- a mixture -- the degree of inner distribution becomes good and the binding capacity between powder which constitutes a mixture is equalized. in addition, the binder which is not contributed to an electromotive reaction -- granularity -- a mixture -- homogeneity distributes in inside. this granularity -- variation does not arise in respect of the cell property of the positive electrode of each pellet type produced in the phase which manufactures a positive electrode using a mixture, i.e., positive-electrode capacity or a discharge property.

[0010] in addition, this invention -- setting -- a positive electrode -- said copolymerization resin in the solution with which fluorinated ethylene-propylene copolymer was distributed so that the weight ratio of the fluorinated ethylene-propylene copolymer to a mixture (positive active material and positive-electrode conductivity matter) might serve as 0.5 - 6% of range -- comparatively -- and the positive electrode of the solution with which/or the aforementioned copolymerization resin was distributed -- it is desirable to adjust the addition to a mixture. the case where the aforementioned weight ratio is 0.5% or less -- granularity -- the absolute magnitude of the fluorinated ethylene-propylene copolymer which exists in a mixture runs short, the binding capacity between powder of positive active material and the positive-electrode conductivity matter is insufficient, and the reinforcement of a pellet serves as imperfection. the case where a weight ratio is 7% or more on the other hand -- fluorinated ethylene-propylene copolymer -- a positive electrode -- the amount welded [which forms a

mixture / each] will increase. It is to cover the reaction front face in each powder of positive active material, and for the reaction utilization factor of a positive electrode to fall by this.
[0011] furthermore, this invention -- setting -- granularity -- as for the particle size of a mixture, it is desirable to set it as the range of 50-1000 micrometers. When this sets up the particle size of a mixture smaller than 50 micrometers, the weighing capacity precision at the time of filling up the metal mold for fabricating to a pellet type will get worse. For this reason, variation will arise in the weight of the positive electrode fabricated, and it will originate in this, and will have an adverse effect on cell capacity etc. Moreover, when the particle size of a mixture is set up more greatly than 1000 micrometers, the specific surface area of positive active material will become small, and the discharge property in a strong load will be reduced.
[0012]
[Example] Next, the example of this invention is explained in full detail.
[0013] (Example 1) The cross-section structure of the flat form cell in this example is shown in drawing 1 .
[0014] In drawing 1 , a positive electrode 1 is kneaded with powder-like positive active material and powder-like electric conduction material, a binder, etc., and is formed in a pellet type. About the creation approach of this positive electrode 1, it mentions later. The negative electrode 2 has the appearance configuration of a pellet type like the positive electrode 1, and formed it by piercing a sheet-like lithium metal circularly. A separator 4 consists of a polypropylene nonwoven fabric which has solution retention, it is arranged between a positive electrode 1 and a negative electrode 2, and impregnation of the organic electrolytic solution is carried out. It is LiPF6 to the mixed solvent of propylene carbonate [which is an aprotic organic solvent at the organic electrolytic solution] and 1, and 2-dimethoxyethane. The solute made into a subject was dissolved, and it prepared so that it might become predetermined concentration. A positive electrode 1, a negative electrode 2, and the organic electrolytic solution considered as the generation-of-electrical-energy element combining the separator 4 in the condition that impregnation was carried out. This generation-of-electrical-energy element held the positive-electrode container 6 which serves as a positive-electrode terminal, and the negative-electrode container 3 which similarly serves as a negative-electrode terminal in the cell container by which seal opening was carried out through the insulating packing 5.
[0015] Next, the creation approach of a positive electrode 1 is explained. It sets to this example and is the powder-like baking MnO2 as positive active material. Moreover, the powder-like graphite was used as conductive matter. Graphite powder was mixed for baking MnO2 at a rate of 6 weight sections to 94 weight sections. the aforementioned positive electrode -- a binder is adjusted in parallel to adjustment of a mixture. After having mixed 20g of distributed solutions of the aquosity polytetrafluoroethylene resin which contains solid content by 60% of the weight of the ratio, and 20g of distributed solutions of the water fluorinated ethylene-propylene copolymer which contains solid content by 50% of the weight of the ratio, stirring and producing a mixed solution, in addition, it fully mixed 200 cc of water further. the obtained mixed solution -- the aforementioned positive electrode -- it added to the mixture and these mixtures and a mixed solution were kneaded.
[0016] the mixed solution of a binder, and the kneaded positive electrode -- performing crushing and a classification, after corning a mixture with a stirring-type granulating machine -- a positive electrode -- the particle size regulation of the mixture was carried out. furthermore, the positive electrode by which the particle size regulation was carried out -- a mixture is dried -- making -- granularity with a diameter of 50-1000 micrometers -- the mixture was obtained. this granularity -- with a press-forming machine, a mixture carries out pressing to a pellet type with a diameter [of 15mm], and a thickness of 2.0mm, and obtains the positive electrode 1 in this example.
[0017] It applied to the generation-of-electrical-energy element and cell container which have the configuration which shows the positive electrode 1 pass like up Noriyuki to drawing 1 , and the flat form cell was created. Let this be Cell A.
[0018] (Example 1 of a comparison) as the example 1 of a comparison -- an example 1 -- the same -- as positive active material -- powder-like baking MnO2 the positive electrode which used the powder-like graphite as conductive matter and mixed these at a rate of 94 weight sections and 6 weight sections -- the mixture was adjusted. Moreover, the distributed solution of the aquosity polytetrafluoroethylene resin which contains solid content by 60% of the weight of the ratio as a binder was used.
[0019] the adjusted positive electrode -- after adding 200 cc of water to 1000g of mixtures, further, 40g was

added and the distributed solution of a binder was kneaded. the desiccation after giving this granulation and a particle size regulation -- carrying out -- granularity with a diameter of 50-1000 micrometers -- this granularity after creating a mixture -- the flat form cell which shows a mixture to drawing 1 like an example 1 with a press-forming machine using the positive electrode by which pressing was carried out to the pellet type with a diameter [of 15mm] and a thickness of 2.0mm was constituted. Let this be Cell B.

[0020] (Example 2 of a comparison) as the example 2 of a comparison -- an example 1 -- the same -- as positive active material -- powder-like baking MnO2 the positive electrode which used the powder-like graphite as conductive matter and mixed these at a rate of 94 weight sections and 6 weight sections -- the mixture was adjusted. Moreover, as a binder, the distributed solution of the aquosity polytetrafluoroethylene resin which contains solid content by 60% of the weight of the ratio, and the distributed solution of the aquosity fluorinated ethylene-propylene copolymer which contains solid content by 50% of the weight of the ratio were used.

[0021] the adjusted positive electrode -- to 1000g of mixtures, 20g of distributed solutions of polytetrafluoroethylene resin and 200 cc of water were added, respectively, and it fully mixed. Then, 50g was added and the distributed solution of fluorinated ethylene-propylene copolymer was kneaded further. the desiccation after giving this granulation and a particle size regulation -- carrying out -- granularity with a diameter of 50-1000 micrometers -- this granularity after creating a mixture -- the flat form cell which shows a mixture to drawing 1 R> 1 like an example 1 with a press-forming machine using the positive electrode by which pressing was carried out to the pellet type with a diameter [of 15mm] and a thickness of 2.0mm was constituted. Let this be Cell C.

[0022] The mechanical strength of a positive electrode and the discharge property of the cell constituted further were examined using the cell A constituted using each positive electrode created in the example 1 and the example of a comparison, and these positive electrodes - Cell C. In here, the drop test estimated as an index for examining the mechanical strength of a positive electrode.

[0023] (1) It created each 100 positive electrodes of the pellet type in the drop test example 1 and the example of a comparison at a time, respectively. Furthermore, it dried by holding this under a 250-degree C temperature ambient atmosphere for 10 hours. The drop test carried out counting of the number of the deformation which was made to carry out free fall of the positive electrode of a pellet type with which desiccation processing was performed on a griddle, performed it from height of 30cm, and produced it in the positive electrode of a pellet type by the impact at the time of drop and a crack, or chips. The result of a drop test is shown in (a table 1).

[0024]

[A table 1]

	電池A	電池B	電池C
割れ、変形の発生数	0個	73個	15個

[0025] The pellet produced in the example 1 so that more clearly than (a table 1) can read that it is few in a crack or the occurrences of deformation in a drop test as compared with the pellet in the example of a comparison. From this, the positive electrode of the pellet type concerning an example 1 has a high mechanical strength compared with the positive electrode in the example of a comparison.

[0026] using fluorinated ethylene-propylene copolymer as binding material as a reason the mechanical strength of the positive electrode in an example 1 is improved -- a positive electrode -- since joining of both the powder that form a mixture is carried out, reinforcement is improving. This is supported by the comparison with the result of the drop test to the positive electrode of the example 1 of a comparison which added polytetrafluoroethylene resin independently.

[0027] this point -- in addition, the condition that polytetrafluoroethylene resin and fluorinated ethylene-propylene copolymer added water further beforehand to the mixed solution with which the solution distributed, respectively was mixed -- setting -- a positive electrode -- a mixture -- adding to inside -- a positive electrode -- the interior of a mixture -- polytetrafluoroethylene resin -- the shape of a blow hole of the spider -- breadth -- further -- simultaneous -- fluorinated ethylene-propylene copolymer -- a positive electrode -- a mixture -- in order to distribute to inside, it is thought that the mechanical strength improved.

[0028] on the other hand, the solution with which, as for the example 2 of a comparison,

polytetrafluoroethylene resin was distributed -- a positive electrode -- after adding to a mixture and fully mixing, the solution with which fluorinated ethylene-propylene copolymer was distributed is added. for this reason, the positive electrode of fluorinated ethylene-propylene copolymer -- a mixture -- distribution of the binder to inside becomes less enough -- in addition, the polytetrafluoroethylene resin added previously -- a mixture -- the mixture of the fluorinated ethylene-propylene copolymer added [to inside] in the shape of [of the spider] a blow hole in breadth and the back -- since the diffusion in inside was checked, it is thought that the effectiveness by addition of fluorinated ethylene-propylene copolymer was not fully demonstrated.
[0029] (2) It produced the cell A in a discharge experiment next the aforementioned example 1, and the example of a comparison - 100 cells C at a time, respectively. Discharge was continued until it connected with the load resistance of 1kohm, it performed continuous discharge and cell voltage arrived at the bottom of a 20-degree C environment to each cell 2.0V. In this discharge, the utilization factor of discharge capacity to positive-electrode capacity until it amounts to 2.0V was computed. The utilization factor of the obtained positive electrode is shown in (a table 2).
[0030]
[A table 2]

	電池A	電池B	電池C
正極の利用率	70%	71%	70%

[0031] The cell A of an example became a positive-electrode utilization factor almost equivalent to the cells B and C of the example of a comparison so that more clearly than (a table 2). therefore, a positive electrode -- the utilization factor of a positive electrode can consider not being influenced according to the class of binder added by the mixture, and a difference of addition sequence.
[0032] in addition, the positive active material which constitutes the positive electrode of a pellet type from this example -- MnO2 although used -- this -- replacing with -- V2 O5 and CuO2 etc. -- a powder-like active material may be used.
[0033]
[Effect of the Invention] as mentioned above, the solution which distributed the dispersion solution and fluorinated ethylene-propylene copolymer of poly TETORAORO ethylene as a binder further after the manufacturing method of the positive electrode for flat form cells of this invention mixed the graphite which are positive active material and the positive-electrode conductivity matter -- mixing -- this -- a positive electrode -- it is considering as the process added to a mixture. Thereby, without worsening the utilization factor of a positive electrode, in the process which the mechanical strength of a positive electrode is raised substantially and inserts a positive electrode in the cell container using an automatic feeder, generating of deformation of a pellet etc. is controlled and the productivity of a flat form cell is raised substantially.

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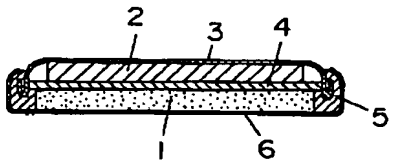
DRAWINGS

[Drawing 1]

1---正極
2---負極
3---負極容器
4---セパレータ
5---絶縁パッキング
6---正極容器



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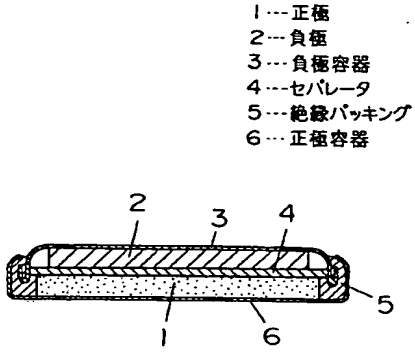
DD01 EE13 EE14

(54)【発明の名称】扁平形電池用正極の製造法

(57)【要約】

【課題】　ペレット状に成形された正極を含む発電要素を、扁平形の電池容器に収容した電池において、ペレット状正極の表面及び内部における割れや欠けの発生、および形状の不具合の発生を抑制する扁平形電池用正極の製造法に関する。

【解決手段】　粉末状の正極活物質、黒鉛を主体とする導電性物質を混合した正極合剤に対して、４フッ化エチレン樹脂が分散された溶液と４フッ化エチレン－６フッ化プロピレン共重合樹脂が分散された溶液とが予め混合された混合溶液を添加することを特徴とする。



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SEARCH REPORT

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【特許請求の範囲】

【請求項１】　正極活物質と、黒鉛を主体とする正極導電性物質とを混合し、正極合剤を形成する工程、４フッ化エチレン樹脂が分散された溶液と、４フッ化エチレン－６フッ化プロピレン共重合樹脂が分散された溶液とを混合して混合溶液とし、この混合溶液に水を添加してさらに混合する工程、水が添加された混合溶液を該正極合剤に添加し、正極合剤を混練する工程、混練された正極合剤を造粒、乾燥し、顆粒状合剤とする工程、顆粒状合剤を型に充填した後、加圧成形してペレット状の正極を形成する工程、からなる扁平形電池用正極の製造法。

【請求項２】　正極活物質及び正極導電性物質に対する４フッ化エチレン－６フッ化プロピレン共重合樹脂の重量比率が、０．５～６重量％である請求項１記載の扁平形電池用正極の製造法。

【請求項３】　顆粒状合剤の粒径が、５０～１０００μｍである請求項１記載の扁平形電池用正極の製造法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、ペレット状に成形された正極を含む発電要素を、扁平形の電池容器に収容した電池の製造法に関し、詳しくはペレット状正極の表面及び内部における割れや欠けの発生を抑制する扁平形電池用正極の製造法に関するものである。

【０００２】

【従来の技術】正極、リチウムあるいはその合金を用いた負極、有機電解質を用いた電解液からなる発電要素を、負極端子を兼ねる封口板、正極端子を兼ねる電池ケースからなる扁平形の電池容器に収容した扁平形有機電解質電池は、負極活物質にリチウムを用いることから、エネルギー密度が高いという特徴を有している。この種の電池は、機器の小型化及び軽量化が可能であるだけでなく、高信頼性を有することから各種電子機器の主電源やメモリーバックアップ電源として使用されている。

【０００３】

【発明が解決しようとする課題】このような扁平形有機電解液電池の正極は、正極活物質及び導電性物質を主体とする導電性二酸化マンガン等の正極活物質と炭素等の導電性物質の粉末とを混合した正極合剤を、造粒・乾燥して顆粒状合剤とした後、これを型に充填、加圧することでペレット状に成形させる方法により作成される。ペレット状の正極は、合剤を加圧のみによって成形しており、合剤を構成する粉末相互の結着力が低い。このため、製造工程における振動、装置との接触あるいはペレット状正極相互の衝突等によって、ペレットの一部が割れ落ちてしまう欠けや、成形後の乾燥によりペレットの内部及び表面に割れが生じてしまう。このような不具合の発生を防止するためには、正極合剤の粘度を上昇させると共に、粉体の結着力を増加させる必要がある。そこで、増粘剤ならびに結着剤として４フッ化エチレン樹脂

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（ＰＴＦＥ）を溶媒中に分散させたディスパージョン溶液を正極合剤に加えて混練した後、ペレット状に成形する方法が用いられている。（例えば、特開昭５５－９３６７１号公報、特開昭５５－９６５５７号公報に記載）上記方法により正極合剤に４フッ化エチレン樹脂を分散させた溶液を添加した製造法では、前記欠けや割れの発生が減少する。しかしながら、ペレット状に成形した後、４フッ化エチレン樹脂を含む溶液が乾燥した際に、変形や反り返りが生じてしまう。このような正極を含む発電要素をパーツフィーダ等の供給機を用いて扁平形の電池容器に収容する際に、ペレット状の正極における変形や反りが生じた部分が供給機内部で引っかかり、電池組み立て工程におけるトラブルの原因となる。

【０００４】本発明は、ペレットに割れや欠けの発生が無く、さらに変形や反りが生じることがない正極を提供することを目的とする。

【０００５】

【課題を解決するための手段】上記目的を達成するために、本発明の扁平形電池用正極の製造法は、粉末状の正極活物質と、同じく粉末状にあり、導電性物質とされる黒鉛とを混合した正極合剤に対して、４フッ化エチレン樹脂が分散された溶液と４フッ化エチレン－６フッ化プロピレン共重合樹脂が分散された溶液とが予め混合された混合溶液に、さらに水を加えた溶液を添加するものであり、４フッ化エチレン－６フッ化プロピレン共重合樹脂が分散された溶液を用いる点、４フッ化エチレン樹脂、及び４フッ化エチレン－６フッ化プロピレン共重合樹脂が分散された各溶液を予め混合した混合溶液を正極合剤に添加する点を特徴としてる。

【０００６】

【発明の実施の形態】以下、本発明の実施形態について、説明する。

【０００７】本発明にかかる扁平形電池用正極の製造法は、以下に示す各工程を含むものである。すなわち、

（１）　粉末状にある正極活物質と、粉末状にあり、且つ黒鉛を主体とする正極導電性物質とを混合し、正極合剤を調整する工程、（２）　４フッ化エチレン樹脂が分散された溶液と、４フッ化エチレン－６フッ化プロピレン共重合樹脂が分散された溶液との混合溶液を作成し、この混合溶液に水を加えた後、さらに混合する工程、

（３）　水が加えられた混合溶液を正極合剤に添加し、正極合剤を混練する工程、（４）　混練された正極合剤を造粒、乾燥し、顆粒状合剤とする工程、（５）　顆粒状合剤を型に充填した後、加圧成形してペレット状の正極を形成する工程、からなる。

【０００８】前記の製造法によれば、正極の結着剤として４フッ化エチレン樹脂、及び４フッ化エチレン－６フッ化プロピレン共重合樹脂を用いており、これらを単独で使用する場合に比べ、正極活物質及び導電物質の結着力が向上する。これによって、顆粒状合剤を加圧、成形

する段階におけるペレットの欠けや割れの発生頻度が大幅に低下する。さらに、成形されたペレット状の正極を、パーツフィーダー等の供給装置を用いて正極容器に供給する工程においても、正極形状の変化、具体的にはペレット主面における反りや潰れといった変形を生じることがない。さらに、変形や反りによる供給機内部での引っかかりが生じることがなく、製造装置の安定した操業に寄与できる。

【０００９】また、各樹脂が分散された溶液を正極合剤に対して別個に添加するのではなく、予め各樹脂が分散された溶液を混合した後、これにさらに水を加えた混合溶液とし、この混合溶液を正極合剤へ添加している。この時、正極合剤中において、前記の各樹脂からなる結着剤の正極合剤中における分散の度合いが良好になり、合剤を構成する粉末相互の結着力が均一化される。加えて、起電反応に寄与しない結着剤は、顆粒状合剤中に均一に分散されている。この顆粒状合剤を用いて正極を製造する段階にて、作製された各ペレット状の正極の電池特性、すなわち正極容量や放電特性の面でもバラツキが生じない。

【００１０】なお、本発明において、正極合剤（正極活物質と、正極導電性物質）に対する４フッ化エチレン－６フッ化プロピレン共重合樹脂の重量比率が、０．５～６％の範囲となるように、４フッ化エチレン－６フッ化プロピレン共重合樹脂が分散された溶液における前記共重合樹脂の割合、および／もしくは前記の共重合樹脂が分散された溶液の正極合剤への添加量を調整するのが好ましい。前記の重量比率が０．５％以下の場合には、顆粒状合剤に存在する４フッ化エチレン－６フッ化プロピレン共重合樹脂の絶対量が不足し、正極活物質及び正極導電性物質の粉末相互の結着力が不足し、ペレットの強度が不十分となる。一方、重量比率が７％以上の場合には、４フッ化エチレン－６フッ化プロピレン共重合樹脂が正極合剤を形成する各粉末に溶着する量が増加してしまう。これにより、正極活物質の各粉末においてその反応表面を被覆してしまい、正極の反応利用率が低下するためである。

【００１１】さらに、本発明において、顆粒状合剤の粒径は、５０～１０００μmの範囲に設定するのが好ましい。これは、合剤の粒径を５０μmより小さく設定した場合には、ペレット状に成形を行うための金型に充填する際の秤量精度が悪化してしまう。このため、成形される正極の重量にバラツキが生じ、これに起因して電池容量等にも悪影響を与えてしまう。また、合剤の粒径が、１０００μmより大きく設定された場合には、正極活物質の比表面積が小さくなり、強負荷における放電特性を低下させてしまう。

【００１２】

【実施例】次に本発明の実施例を詳述する。

【００１３】（実施例１）本実施例における扁平形電池の断面構造を図１に示す。

【００１４】図１において、正極１は、粉末状の正極活物質、及び粉末状の導電材、結着剤等と混練し、ペレット状に形成している。この正極１の作成方法については、後述する。負極２は、正極１と同様にペレット状の外観形状を有しており、シート状のリチウム金属を円形に打ち抜くことで形成した。セパレータ４は、保液性を有するポリプロピレン不織布からなり、正極１と負極２との間に配置され、有機電解液が含浸されている。有機電解液には、非プロトン性有機溶媒であるプロピレンカーボネート、及び１，２－ジメトキシエタンの混合溶媒に、$LiPF_6$ を主体とする溶質を溶解しており、所定の濃度となるように調製した。正極１、負極２及び有機電解液が含浸された状態にあるセパレータ４を組み合わせて発電要素とした。この発電要素は、正極端子を兼ねる正極容器６、同じく負極端子を兼ねる負極容器３を絶縁パッキング５を介して密封口された電池容器に収容した。

【００１５】次に正極１の作成方法について説明する。本実施例においては、正極活物質として、粉末状の焼成 MnO_2 を、また導電性物質として粉末状の黒鉛を用いた。焼成 MnO_2 を９４重量部に対して、黒鉛粉末を６重量部の割合で混合した。前記の正極合剤の調整に並行して、結着剤の調整を行う。固形分を６０重量％の比率にて含む水性４フッ化エチレン樹脂の分散溶液２０ｇと、固形分を５０重量％の比率にて含む水性の４フッ化エチレン－６フッ化プロピレン共重合樹脂の分散溶液２０ｇとを混合、撹拌して混合溶液を作製した後、さらに水２００ｃｃ加えて充分に混合した。得られた混合溶液を、前記の正極合剤に添加し、これら合剤と混合溶液を混練した。

【００１６】結着剤の混合溶液と混練された正極合剤を、撹拌式の造粒機によって造粒した後、破砕、分級を施すことで正極合剤を整粒した。さらに、整粒された正極合剤を乾燥させて、直径５０～１０００μmの顆粒状合剤を得た。この顆粒状合剤は、プレス成形機によって、直径１５mm、厚さ２．０mmのペレット状に加圧成形し、本実施例における正極１を得る。

【００１７】上記行程を経て得られた正極１を、図１に示す構成を有する発電要素及び電池容器に適用し、扁平形電池を作成した。これを電池Ａとする。

【００１８】（比較例１）比較例１として、実施例１と同様に正極活物質として粉末状の焼成 MnO_2 を、導電性物質として粉末状の黒鉛を使用し、これらを９４重量部、６重量部の割合で混合した正極合剤を調整した。また、結着剤として固形分を６０重量％の比率にて含む水性４フッ化エチレン樹脂の分散溶液を用いた。

【００１９】調整された正極合剤１０００ｇに、水２００ｃｃを加えた後、さらに結着剤の分散溶液を４０ｇを添加して混練した。これに造粒及び整粒を施した後、乾

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燥を行い直径５０～１０００μmの顆粒状合剤を作成した後、この顆粒状合剤をプレス成形機によって、直径１５mm、厚さ２．０mmのペレット状に加圧成形された正極を用いて、実施例１と同様に図１に示す扁平形電池を構成した。これを、電池Ｂとする。

【００２０】（比較例２）比較例２として、実施例１と同様に正極活物質として粉末状の焼成MnO_2を、導電性物質として粉末状の黒鉛を使用し、これらを９４重量部、６重量部の割合で混合した正極合剤を調整した。また結着剤として、固形分を６０重量％の比率にて含む水性４フッ化エチレン樹脂の分散溶液と、固形分を５０重量％の比率にて含む水性４フッ化エチレン－６フッ化プロピレン共重合樹脂の分散溶液を用いた。

【００２１】調整された正極合剤１０００ｇに対して、４フッ化エチレン樹脂の分散溶液２０ｇ、水２００ｃｃをそれぞれ加え、充分に混合した。この後、さらに４フッ化エチレン－６フッ化プロピレン共重合樹脂の分散溶液を５０ｇを添加し、さらに混練した。これに造粒及び整粒を施した後、乾燥を行い直径５０～１０００μmの顆粒状合剤を作成した後、この顆粒状合剤をプレス成形機によって、直径１５mm、厚さ２．０mmのペレット

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状に加圧成形された正極を用いて、実施例１と同様に図１に示す扁平形電池を構成した。これを、電池Ｃとする。

【００２２】実施例１、比較例において作成された各正極、及びこれら正極を用いて構成された電池Ａ～電池Ｃを用いて、正極の機械的強度、さらに構成された電池の放電特性について検討を行った。ここにおいて、正極の機械的強度を検討するための指標としては、落下試験にて評価を行った。

【００２３】（１）　落下試験

実施例１及び比較例におけるペレット状の各正極を、それぞれ１００個ずつ作成した。さらに、これを２５０℃の温度雰囲気下に１０時間保持することによって乾燥を施した。落下試験は、乾燥処理が施されたペレット状の正極を、３０cmの高さから、鉄板上に自由落下させて行い、落下時の衝撃によりペレット状の正極に生じた変形、及び割れや欠けの数を計数した。落下試験の結果を（表１）に示す。

【００２４】

【表１】

	電池Ａ	電池Ｂ	電池Ｃ
割れ、変形の発生数	０個	７３個	１５個

【００２５】（表１）より明らかなように実施例１において作製されたペレットは、比較例におけるペレットに比較して、落下試験にて割れや変形の発生数が少ないことが読みとれる。このことから、実施例１にかかるペレット状の正極は、比較例での正極に比べて、高い機械的強度を有する。

【００２６】実施例１における正極の機械的強度が改善される理由としては、結着材として４フッ化エチレン－６フッ化プロピレン共重合樹脂を用いることにより、正極合剤を形成する粉末相互が溶着されるために、強度が向上している。このことは、４フッ化エチレン樹脂を単独にて添加した比較例１の正極に対する落下試験の結果との比較によって裏付けられる。

【００２７】この点に加えて、予め４フッ化エチレン樹脂、及び４フッ化エチレン－６フッ化プロピレン共重合樹脂がそれぞれ分散された溶液を混ぜ合わせた混合溶液に、さらに水を添加した状態において、正極合剤中に加えることによって、正極合剤の内部に４フッ化エチレン樹脂がクモの巣状に広がり、さらに同時に４フッ化エチレン－６フッ化プロピレン共重合樹脂も正極合剤中に分散するために、機械的強度が向上したと考えられる。

【００２８】これに対して比較例２は、４フッ化エチレン樹脂が分散された溶液を正極合剤に添加し、充分に混合した後に、４フッ化エチレン－６フッ化プロピレン共重合樹脂が分散された溶液を添加している。このため、４フッ化エチレン－６フッ化プロピレン共重合樹脂の正極合剤中への結着剤の分散が充分でなくなることに加えて、先に添加された４フッ化エチレン樹脂が合剤中へクモの巣状に広がり、後で添加される４フッ化エチレン－６フッ化プロピレン共重合樹脂の合剤中での拡散を阻害したため、４フッ化エチレン－６フッ化プロピレン共重合樹脂の添加による効果が充分に発揮されなかったと考えられる。

【００２９】（２）　放電実験

次に前記の実施例１及び比較例における電池Ａ～電池Ｃを、それぞれ１００個づつ作製した。各電池に対して、２０℃の環境下において、１kΩの負荷抵抗に接続して連続放電を行い、電池電圧が２．０Ｖに達するまで放電を継続した。この放電において、２．０Ｖに達するまでの放電容量から、正極容量の利用率を算出した。得られた正極の利用率を（表２）に示す。

【００３０】

【表２】

	電池A	電池B	電池C
正極の利用率	70%	71%	70%

【００３１】（表２）より明らかなように実施例の電池Aは、比較例の電池B、Cとほぼ同等の正極利用率となった。従って、正極合剤に添加される結着剤の種類、及び添加順序の相違によって、正極の利用率は影響を受けないことが考えられる。

【００３２】尚、本実施例ではペレット状の正極を構成する正極活物質に、MnO_2 を用いたが、これに代えて V_2O_5 、CuO_2 等の粉末状の活物質を用いても良い。

【００３３】

【発明の効果】以上のように、本発明の扁平形電池用正極の製造法は、正極活物質と正極導電性物質である黒鉛を混合した後、さらに結着剤としてポリテトラオロエチレンのディスパージョン溶液と４フッ化エチレン－６フッ化プロピレン共重合樹脂を分散した溶液を混合し、これを正極合剤に添加する工程としている。これにより、正極の利用率を悪化させることなく、正極の機械的強度を大幅に向上させており、自動供給機を用いての電池容器へ正極を挿入する工程において、ペレットの変形等の発生を抑制し、扁平形電池の生産性を大幅に向上させるものである。

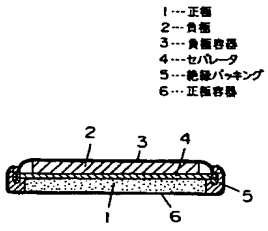
【図面の簡単な説明】

【図１】本実施例における扁平形電池の断面構造を示す図

【符号の説明】

1　正極
2　負極
3　負極容器
4　セパレータ
5　絶縁パッキング
6　正極容器

【図１】



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